

Please amend claim 17 as follows:

I2
17. (Amended) The method as claimed in claim 1 [and] in which [comprises]
said method is for retaining transformer oil on a paper.

[Please amend claim 22 as follows:]

I3
22. (Amended) A sheet of lignocellulosic plant material which has been modified
by esterification of hydroxyl groups in the lignin of the lignocellulose material such as to
render the material [rendered relatively] more attractive to hydrophobic water-immiscible
liquids [by esterification of hydroxyl groups in the lignin of the plant material] while still
retaining hydrogen bonding to maintain the structural integrity of the material..

REMARKS

Reconsideration of the above-identified patent application, as amended, is respectfully requested. Applicant has amended the claims to overcome a 112 rejection to claim 17 and to further clarify the independent claims 1 and 22. It is submitted that the claims are now in condition for allowance.

The present invention relates to methods of absorbing hydrophobic water-immiscible liquids (e.g. oil spillages) using a lignocellulosic plant material which has been subjected to esterification (discussed more fully below). The preferred esterification is acetylation, although other esterifying groups are contemplated, e.g. as set out towards the bottom of page 2 of the specification. The application specifically discloses an acetylation technique which is along the lines of that set out in EP-A-0 213 352. This is a relatively mild esterification technique which produces a material having two characteristics which are important in the context of the present invention.

First, the lignin material remains a part of the chemical structure of the plant material in a form that is available for acetylation as an integral part of the structure. In other words, the lignin is not only retained in the material but is retained in a form in which it is capable of being acetylated. The presence of the lignin results in a higher weight gain as a result of the acetylation reaction than would be the case if the acetylation procedure converted the lignin into a form in which it could not be acetylated (since in the former case there are more hydroxyl groups available for acetylation).

Second, the acetylation procedure ensures that the hydrogen bonds which maintain the structural integrity of the lignocellulosic material are not destroyed to an extent that the structural morphology is changed.

The first feature is important because the weight gain is a function of the number of hydrophobic acetyl groups introduced into the material. The greater the weight gain (and the number of acetyl groups) the greater is the hydrophobicity of the acetylated material. Acetylated materials used in accordance with the invention are more hydrophobic than the prior art materials due to the greater weight gain obtained by acetylation of the lignin.

The second feature is important because the absorbency of cellulosic and lignocellulosic materials (for liquids) is due to the porous structure and high surface area of the whole material. This is seen by the high liquid uptake of unmodified lignocellulosic fibers as set out in Examples 2 and 5 of the present specification. The second feature outlined above ensures that the porous structure of the material is retained and therefore its ability to absorb many times its own weight in liquid.

It is the combination of the increased number of hydrophobic acetyl groups coupled with the retention of the hydrogen bonding (to obtain the porous structure) which together lead to a material which is particularly effective for removal of oil (and other hydrophobic water immiscible liquids).

An additional point is that in accordance with the invention the preferred lignocellulosic material to be acetylated is in the form of fibers most preferably thermomechanically pulped (TMP) fibers. Untreated lignocellulosic fibers have a lignin rich outer surface. It is also possible to produce TMP fibers while maintaining a lignin rich outer surface. Acetylation of such fibers in accordance with the invention therefore produces a material having a large number of hydrophobic acetyl groups in the outer regions of the fibers precisely where the groups are required for the "pick-up" of water immiscible hydrophobic liquids.

The following experimental results support the arguments set out above. Two acetylated materials were produced from TMP softwood fiber (of the type used in Example 1 of the present application) as a lignin rich starting material. As a sample comparison, one of the acetylated materials was produced by following the method of Example VI of Teng (but acetylated material was produced using the procedure described in Example 1 of the present application with TMP softwood fiber (impregnated with liquid acetic anhydride) being reacted at 120°C for 2 hours.

The resulting products were then used in the method of Example 2 of the present application for determining their ability to absorb transformer oil. The results are as follows:

Method	Material	Weight gain due to acetylation	Oil/Water weight gain by fibers*	%Oil	%Water
Teng	TMP	5.1	14.7	51.2	48.8
Invention	TMP	17.4	19.9	73.5	26.5

*Multiple of initial fiber weight.

The acetylation in accordance with the invention provided a weight gain of 17.4% whereas the Teng material gave a weight gain of only 5.1%. Thus a greater number of acetyl groups were introduced into the lignocellulosic material using the method of the invention than the Teng method. This demonstrates then that the acetylation method used in the invention is able to acetylate the lignin. Further, the material produced in accordance with the present invention gave a greater pick up (19.9) of the oil/water mixture than the product prepared by the Teng method (14.7).

The final two columns of the table demonstrate that the material in accordance with the invention is preferentially more oil absorbent than that produced by the Teng method. This is a function of the chemical nature of the materials and reflects the fact that the material produced in accordance with the invention has a greater degree of acetylation (provided by the acetylated lignin groups).

Sohnius describes an "Oil Slick Removal System" which comprises finely divided oil absorptive/adsorptive cellulosic material interspersed with a water-repellant agent, e.g. of the type described at column 2, line 23 et seq. of Sohnius. It is apparent that the cellulosic material used by Sohnius is "chemically treated" but is not in fact "chemically modified" as it is really just coated with a water repellent mixture. The Examiner clearly recognizes that Sohnius does not disclose the present invention but argues that it would

be obvious to replace the treated cellulosic material of Sohnius by the lignocellulosic product of Brink to arrive at the present invention.

Brink relates to the production of molded products from lignocellulosic particulate materials (see for example column 1, lines 58-68 of Brink). The first step of the Brink process is oxidation of the particulate material. In the preferred embodiment of Brink this is effected using nitric acid (see column 2, lines 12 et seq.) although oxidation with oxygen is also contemplated (see column 4, lines 32 et seq.). The aim of the oxidation is to generate, in the lignocellulose, functional groups which may take part in a cross-linking reaction during the subsequent molding step. Thus, with reference to oxidation by nitric acid, it is stated at column 4, lines 24-30 that a primary purpose of the oxidation is to provide the lignocellulosic material with carboxyl groups. Similar comments apply to oxidation by oxygen.

Up to this point, the "treated" particulate lignocellulosic material of Brink is different from that employed in the present invention. Thus, in the present invention, the hydroxyl groups of the lignin are "capped" with hydrophobic groups so as to produce a material which is preferentially more absorbent to hydrophobic water-immiscible liquid as compared the original cellulosic material. In contrast, Brink is breaking open the sugar units of the lignocellulosic material. This is demonstrated for oxidation of glucose by nitric acid in the enclosed copy pages from a textbook entitled "Organic Chemistry" by John McMurray (Brooks/Cole Publishing Co. 1984). The enclosed pages show the effect of *dilute* nitric acid. Column 2, line 44 of Brink discloses that the particulate lignocellulosic material to be treated may consume from about 2.5 to 50 wt% nitric acid. The resultant opened structures with reactive acid groups would, in fact, be more

hydrophilic than the original particulate lignocellulosic material. Thus, a number of differences may be identified with regard to present claim 1. First, from the chemical point of view the material as defined in present claim 1 with its “capped” hydroxyl group is different from the Brink product which has been “relatively more absorbent to hydrophobic water-immiscible liquids” (as compared to the starting lignocellulosic material) as required by present claim 1 – it would in fact be more hydrophilic. Thirdly, the Brink method will have lost its structural integrity.

Brink’s oxidized, particulate lignocellulosic material is then used for producing a molded product. During molding, cross-linking occurs within the treated particulate lignocellulosic material, e.g. as described at column 5, line 2 et seq. Examples of cross-linking reactions include esterification. It seems to be on this basis that the Examiner concludes that the Brink material is the same as that defined in claim 1 of the present application. This is not the case.

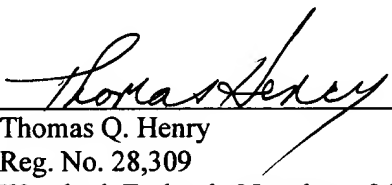
The only “common” feature between the molded product of Brink and the material defined in present claim 1 is “esterification”. Otherwise, the two materials are completely different. Brink’s molded product may, for example, be a particle board (see column 10, line 19 et seq.) and in any of its forms the molded product would be totally unsuitable for absorbing hydrophobic water-immiscible liquids. The Examiner has focused on the reference in column 1, line 14 of Brink that his molded product has “resistance to moisture”. The latter term is however relative and does not imply hydrophobicity. There is no possibility that the solid, molded product would be an effective material for absorbing hydrophobic water-immiscible liquids (e.g. for cleaning

up oil spills) because of its minimal surface area, as compared to the product of the invention which has maintained structural integrity.

Still less is there any suggestion in Brink that the applicant's preferred material, in which the hydroxyl groups of the lignin are acetylated, would be useful for absorbing hydrophobic water-immiscible liquids.

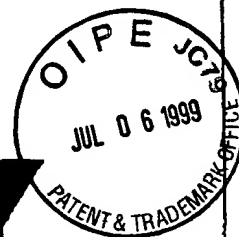
For the foregoing reasons and in view of the amendments made herein, applicant submits that the claims are in condition for allowance.

Respectfully submitted,

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ORGANIC CHEMISTRY

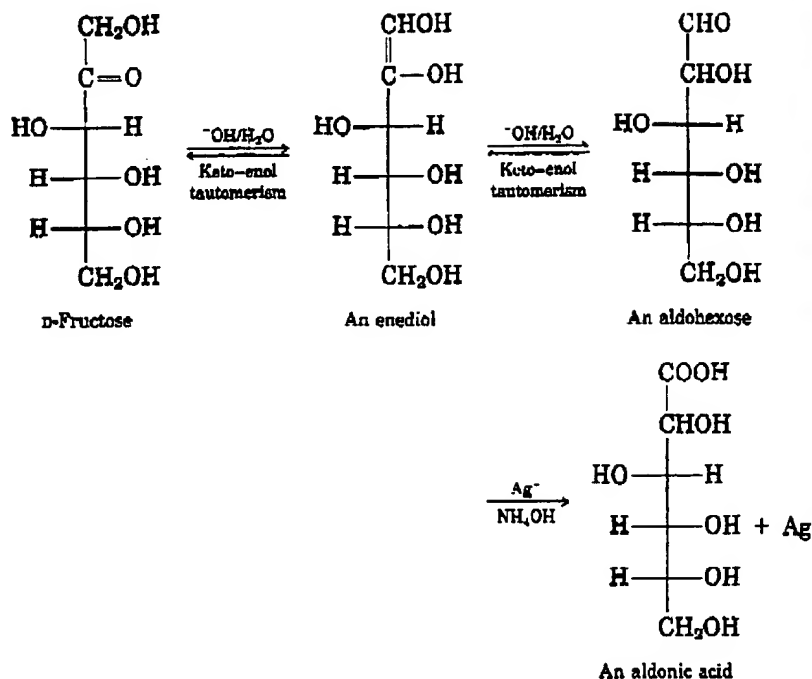


JOHN MCMURRY *Cornell University*

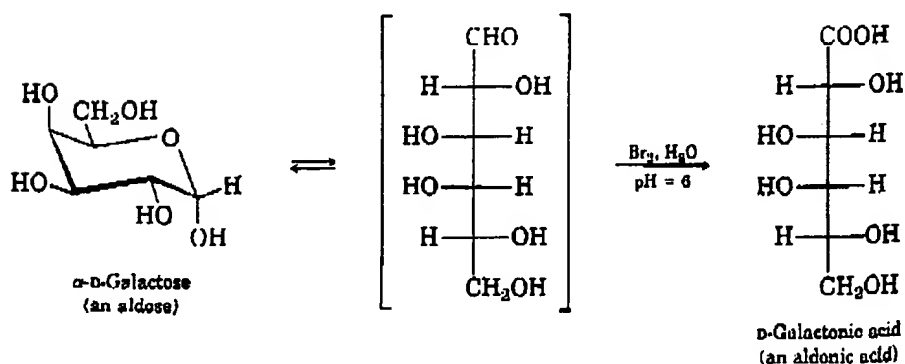
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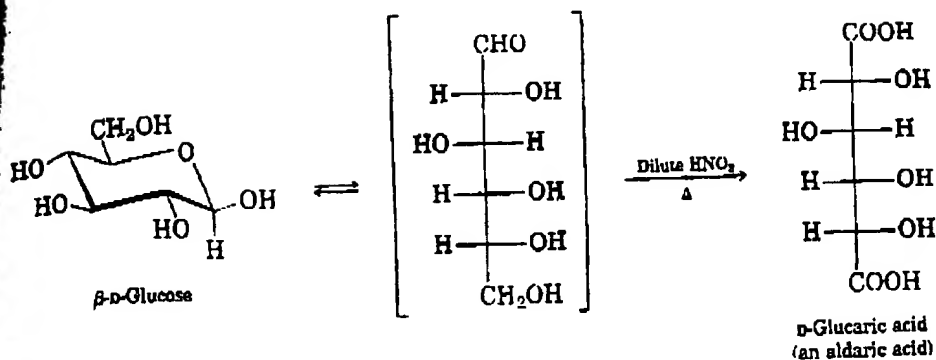


Although both the Tollens and Fehling reactions serve as useful tests for reducing sugars, they do not give good yields of carboxylic acid products because the alkaline conditions used cause decomposition of the carbohydrate skeleton. It has been found, however, that a buffered solution of aqueous bromine oxidizes aldoses to aldonic acids in high yield. The reaction is specific for aldoses; ketoses are not oxidized by bromine water.



If a more powerful oxidizing agent such as warm dilute nitric acid is used, aldoses are oxidized to aldaric acids. Both the aldehyde group at C1 and the terminal $-\text{CH}_2\text{OH}$ group are oxidized in this reaction, and a diacid results:

27.8 REACTIONS OF MONOSACCHARIDES 901



The various kinds of carbohydrate derivatives are shown in Figure 27.9.

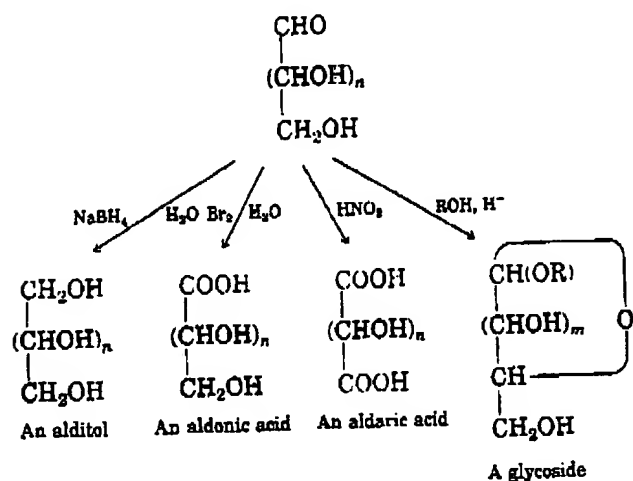


Figure 27.9. Summary of carbohydrate derivatives.

PROBLEM

- 27.13 Which of the eight D-aldoheptoses lead to optically active aldonic acids on oxidation, and which lead to meso aldonic acids?

CHAIN LENGTHENING: THE KILIANI-FISCHER SYNTHESIS

Much early activity in carbohydrate chemistry was devoted to unraveling the various stereochemical relationships among monosaccharides. One of the methods used was the Kiliani-Fischer synthesis. Heinrich Kilian⁵

⁵Heinrich Kiliani (1855-1945); b. Würzburg, Germany; Ph.D. Munich (Erlenmeyer); professor, University of Freiburg.